PB-236 930

COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (NITRIC ACID PLANTS)

Henry F. Hamil, et al

Southwest Research Institute

Prepared for:

Environmental Protection Agency

8 May 1974

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TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)*		PB 236 930
1. REPORT NO. EPA-650/4-74-028	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants)		5. REPORT DATE May 1974 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Henry F. Hamil and R. E. Thomas		8. PERFORMING ORGANIZATION REPORT NO. Project No. 01-3462-004
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute 8500 Culebra Road San Antonio, Texas 78284		10. PROGRAM ELEMENT NO. 1HA327 11. CONTRACT/GRANT NO. 68-02-0626
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency Methods Standardization & Performance Evaluation Branch National Environmental Research Center Research Triangle Park, N. C. 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

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The test was conducted at a nitric acid plant using 4 collaborating laboratories. A total of 22 samples were taken over a 3-day period. In addition, standard gas samples were taken and nitrate solutions whose true concentrations were unknown to the collaborators were prepared for concurrent analysis. The concentrations determined by the collaborators from all three phases of the test were submitted to statistical analysis to obtain estimates of the accuracy and precision that can be expected with the use of Method 7.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	41
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $3.75 - 2.25

EPA Form 2220-1 (9-73)

SOUTHWEST RESEARCH INSTITUTE
Post Office Drawer 28510, 8500 Culebra Road
San Antonio, Texas 78284

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by
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EPA Contract No. 68-02-0626
SwRI Project No. 01-3462-004

Prepared for
Methods Standardization and Performance Evaluation Branch
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May 8, 1974

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SUMMARY AND CONCLUSIONS

This report presents the results obtained from a collaborative test of Method 7 promulgated by the Environmental Protection Agency for determining the nitrogen oxide emissions from stationary sources. Method 7 specifies the collection of a grab sample in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution and the colorimetric measurement of the nitrogen oxides, except nitrous oxide, using the phenoldisulfonic acid procedure.

The test was conducted at a nitric acid plant using four collaborating laboratories. A total of 22 samples were taken over a three-day period. In addition, standard gas samples were taken, and nitrate solutions whose true concentrations were unknown to the collaborators were prepared for concurrent analysis. The concentrations determined by the collaborators from all three phases of the test were submitted to statistical analysis to obtain estimates of the accuracy and precision that can be expected with the use of Method 7.

The statistical analysis provides the basis for the following conclusions:

Accuracy—Samples of standard gas mixtures at three concentrations, 107, 344, and 784 ppm, were taken and analyzed according to Method 7. Using the values determined by the collaborators, we can say that the method is accurate at the 95 percent level of confidence.

Precision—The precision of Method 7 is given in terms of within-laboratory and between-laboratory components and a laboratory bias component. The precision estimates are derived from the stack concentration determinations, with some adjustment. Due to plant upset, there was considerable variation in the actual NO_x concentrations in the stack during the first day's sampling. The fluctuation was reflected in the NO_x concentrations values obtained by the collaborators and necessitated a correction in the data for the fluctuating mean. However, the net effect likely left the precision estimates obtained higher than the actual precision values. The precision components are shown to be proportional to the mean of the Method 7 determinations, given by δ, and can be summarized as follows:

(a) Within-laboratory: The estimated within-laboratory standard deviation is 14.88% of δ, and has 67 degrees of freedom associated with it.

(b) Between-laboratory: The estimated between-laboratory standard deviation is 18.47% of δ, with 3 degrees of freedom.

(c) Laboratory bias: From the above, we can estimate a laboratory bias standard deviation of 10.49% of δ.

Analytical Procedure—The unknown nitrate solution data provides a basis for measuring the accuracy and precision of the analytical procedure taken by itself. At three levels of concentration, the procedure is shown to be accurate at the 95 percent level of confidence. The within-laboratory standard deviation is not a function of the concentration, μ, and is estimated as 1.199 μg/mℓ. The laboratory bias standard deviation is a linear function of the true concentration and is estimated by $0.725 + (0.092)\mu$. From an analysis of variance, the only consistently significant factor affecting the precision of the concentrations obtained is the day-to-day variations within a given laboratory. This implies a need for recalibration of the spectrophotometer on a daily basis to negate the effect on the values of drift.

Recommendations are made for the improvement of the precision of Method 7, and considerations given for the use of the method in field testing.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3462-004, Contract No. 68-02-0626, which includes collaborative testing of Method 7 for nitrogen oxide emissions as given in "Standards of Performance for New Stationary Sources."[2]

This report describes the collaborative testing of Method 7 in a nitric acid plant, the statistical analysis of the data from the collaborative tests, and the conclusions and recommendations based on the analysis of data.

II. COLLABORATIVE TESTING

A. Collaborative Test Site

The collaborative test of Method 7 in a nitric acid plant was conducted at Mobay Chemical Company, Baytown, Texas. The nitric acid unit at Mobay Chemical Company utilizes a proprietary process in which ammonia is catalytically oxidized. Due to the proprietary nature of the process, no information concerning production rates, operational parameters, or unit design could be made available to Southwest Research Institute by Mobay Chemical Company for publication. Emission data from the unit on-stream analyzer indicated normal NO_x concentration in the vent gas duct (Figure 1) leading to the stack to be in the range of 200-250 ppm. We were assured by plant personnel that this NO_x concentration placed them below the maximum permissable emission levels specified by the New Source Performance Standards for nitric acid plants.[2]

In Figure 1 is shown the configuration of the tail gas vent leading into the vertical stack and the configuration of the sampling manifold. The sample manifold consisted of a ten-foot length of 2-inch ID stainless steel tubing, fitted with four sample outlet valves (Whitey® toggle valves) spaced at two-foot centers. The sample valves were installed in the sample manifold in such a manner as to have the sample inlet at the centroid of the sample manifold. The sample manifold was fitted with a stainless steel gauze diffuser 2 inches from the 1/2-inch tubing sample inlet line, in order to provide a mixing zone to prevent channeling of the incoming sample. The sample manifold was connected through a valve to the tail gas vent by means of a 1/2-inch stainless steel line. The sample manifold connection was at a point approximately three feet downstream from the sample takeoff for the on-stream analyzer.

The tail gas vent on the unit was maintained at 3-4 psig which provided sufficient pressure head to provide a high sample flow rate through the sample manifold. The sample manifold was continually purged with a moderate sample flow during the course of a day's sampling. Approximately two minutes before a sample was taken, the sample flow rate was increased to a high flow rate to assure that the gas in the sample manifold was representative of the gas in the tail gas vent. The exhaust gas from the sample manifold was exhausted to atmosphere through a hydrogen peroxide bubbler to scrub out nitrogen oxides. Figure 2 shows the test setup at Mobay, while Figure 3 shows the collaborators taking a sample.

The original collaborative test plan called for each collaborator to collect six samples (rotating among sample points) on each of four days. However, on the first day of sampling, a minor explosion, caused by rupture of a high pressure gas line, occurred in another unit in the plant. Since the nitric acid produced at Mobay is used internally as an intermediate in other processes, it was necessary for plant personnel to reduce the nitric acid production. Only limited storage space in one nitric acid tank was available to accept continued production. Arrangements were made with Mobay to reduce the production rate in order that two more days of sampling could be conducted. As a result, six samples were taken on the first day, and eight samples were taken on the second and third days, respectively. On the fourth day, gas standard samples were taken by the collaborators at the SwRI Houston laboratory. The gas standard samples were prepared at the time of sampling by personnel from the National Bureau of Standards. The gas standard preparation train is shown schematically in Figure 4. The method used for producing the nitric oxide in air standards consisted of metering a controlled, known small amount of a 0.98 mole percent NO in N_2 mixture into an air stream flowing at a known and much higher flow rate. The mixture passed through two mixing chambers and into a sampling manifold from which the collaborators took their samples.

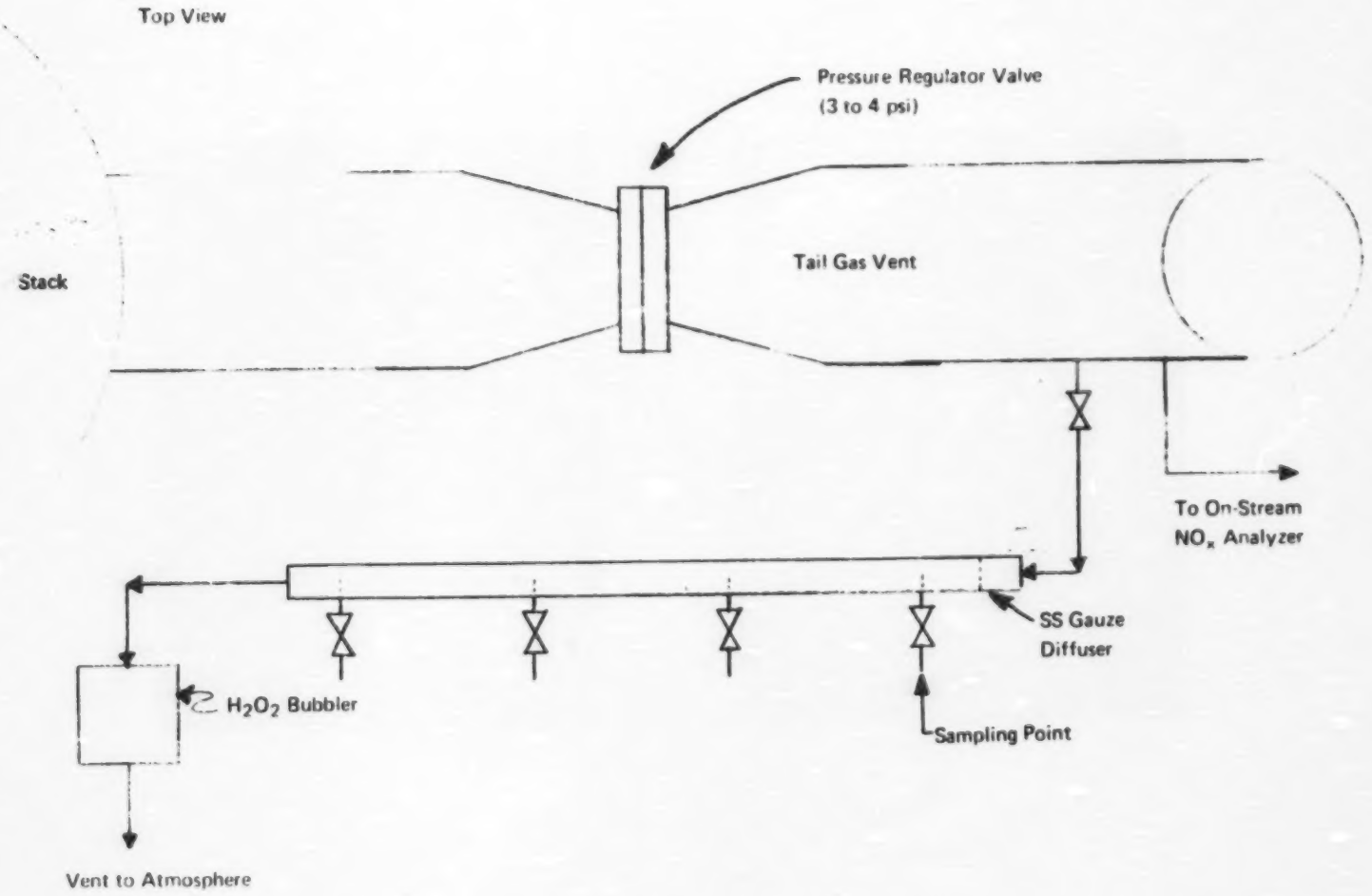

FIGURE 1. TAIL GAS VENT LINE AND SAMPLE MANIFOLD.

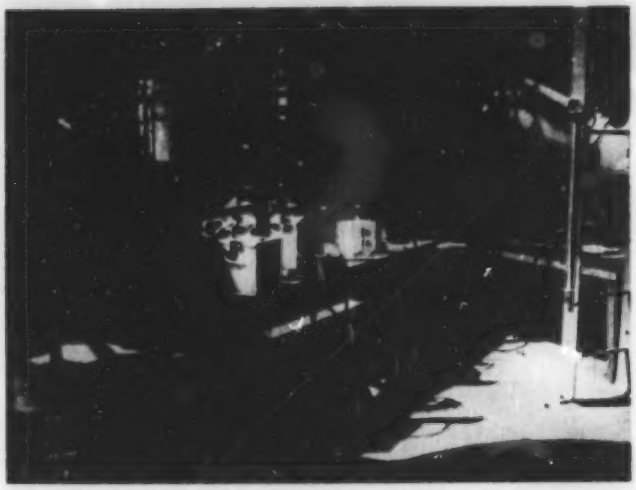

FIGURE 2. TEST SETUP AT MOBAY CHEMICAL COMPANY TEST SITE.

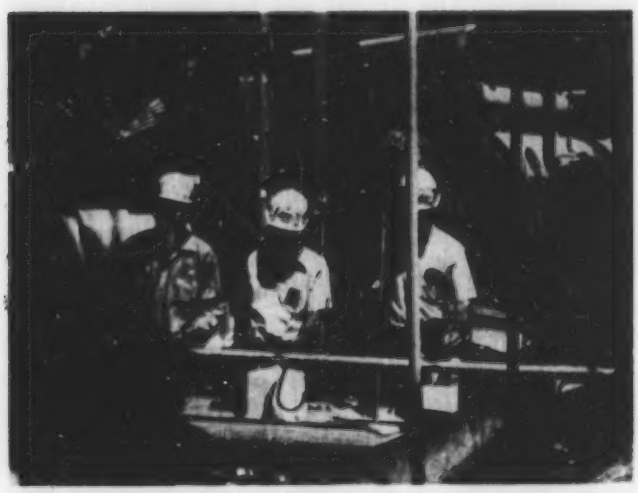

FIGURE 3. COLLABORATORS SAMPLING AT THE MOBAY CHEMICAL COMPANY TEST SITE.

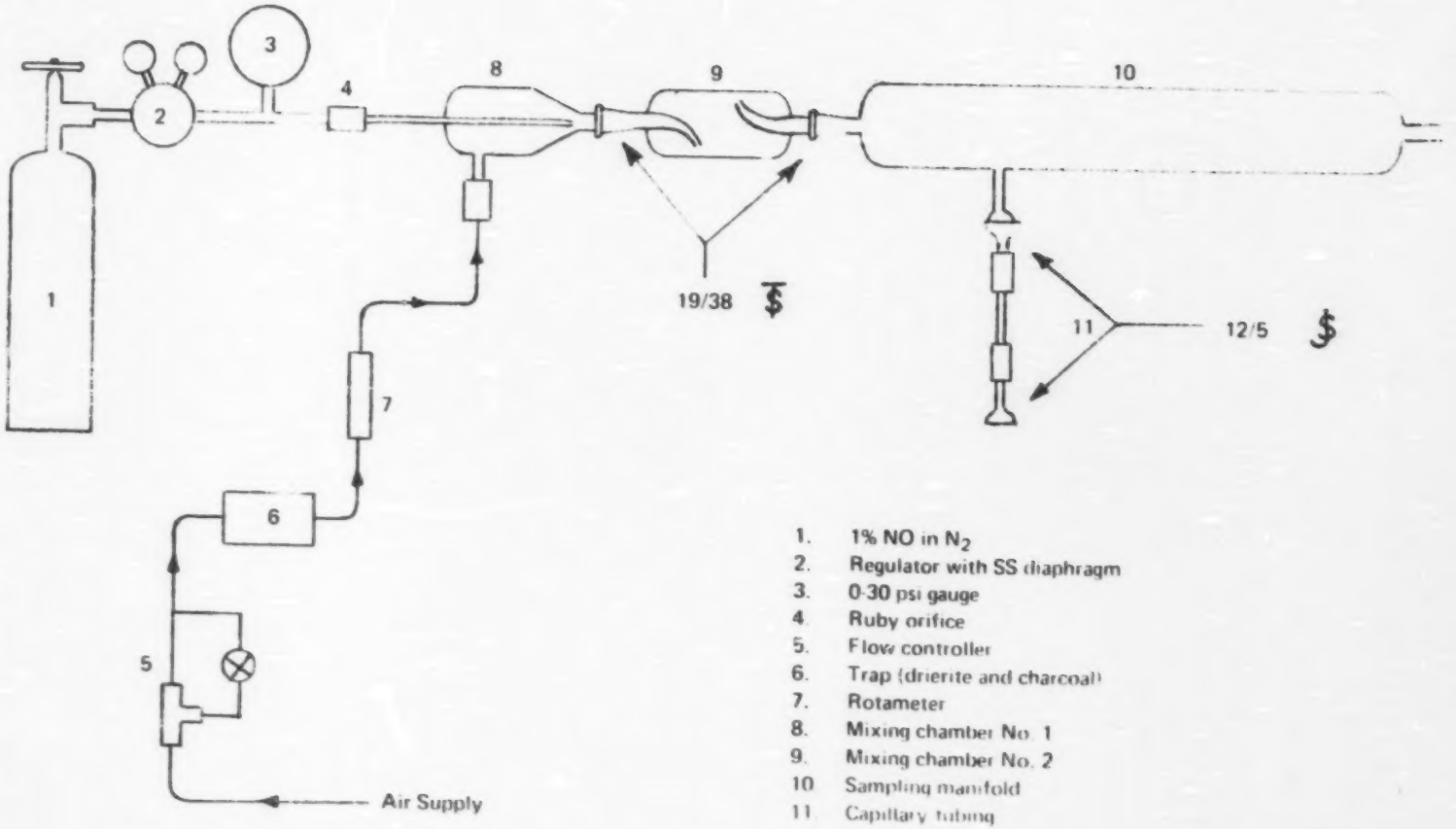

FIGURE 4. SCHEMATIC OF GAS STANDARD SAMPLE PREPARATION TRAIN

Three concentration levels of nitrogen oxide standards were generated, and the collaborators took three samples of each standard.

B. Collaborators and Test Personnel

The collaborators for the Mobay nitric acid plant test were Dr. Robert James and Mr. Thomas Jay McMickle, Texas Air Control Board, State of Texas, Messrs. Quirino Wong and Randy Creighton, Department of Public Health, City of Houston, Houston Texas, Mr. Mike Taylor, Southwest Research Institute, Houston Laboratory, Houston, Texas and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas.*

The standard gas samples were prepared and the concentrations verified under the supervision of Mr. William D. Dorko, Chemist, Air Pollution Analysis Section, Analytical Chemistry Division, The National Bureau of Standards, Washington, D.C.

The collaborative test was conducted under the supervision of Mr. Nollie Swynnerton of Southwest Research Institute. Mr. Swynnerton had the overall responsibility for assuring that the collaborators were competent to perform the test, that the test was conducted in accordance with the collaborative test plan, and that all collaborators adhered to Method 7 as written in the *Federal Register*.[2]

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision and without any additional information from outside sources, i.e. test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of absorbing solution, improper rinsing of flasks, etc., no interference was made by the test supervisor. Since such random errors will occur in the every day use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the field test results which will be obtained when the method is put into general usage. However, if gross deviations were observed, of such magnitude as to make it clear that the collaborator was not following the method as written, these would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgement as to the interpretation of the instructions.

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability and precision of the method that would be expected in performance testing in the field.

*Throughout the remainder of this report, the collaborative laboratories are referenced by assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not necessarily correspond to the above ordered listing of collaborators.

III. STATISTICAL DESIGN AND ANALYSIS

A. Statistical Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The procedures for obtaining estimates of the pertinent values are developed and justified in the subsequent sections.

We say that an *estimator*, $\hat{\theta}$, *is unbiased for a parameter* θ if the expected value of $\hat{\theta}$ is θ, or in notational form, $E(\hat{\theta}) = \theta$. Let $x_1, x_2, \ldots, x_n$ be a sample of n replicate method determinations. Then we define:

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean*, an unbiased estimate of the *true mean*, δ, *of the determinations*. This term gives an estimate of the center of the distribution of the x_i's.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2$ as the *sample variance*, an unbiased estimate of the *true variance*, σ^2. This term gives a measure of the dispersion in a distribution.

(3) $s = \sqrt{s^2}$ as the *sample standard deviation*, an alternative measure of dispersion, which estimates σ, the *true standard deviation*.

The sample standard deviation, s, however, is not unbiased for σ,[1] so a *correction factor* needs to be applied. The correction factor for a sample of size n is α_n, and the product of α_n and s is unbiased for σ. That is, $E(\alpha_n s) = \sigma$. As n increases, the value of α_n decreases, going for example from $\alpha_3 = 1.1284$, $\alpha_4 = 1.0854$ to $\alpha_{10} = 1.0281$.

We define

$$\beta = \frac{\sigma}{\delta}$$

as the *true coefficient of variation* for the distribution of the method determinations. To estimate this parameter, we use a *sample coefficient of variation*, $\hat{\beta}$, defined by

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

where $\hat{\beta}$ is the ratio of the unbiased estimates of σ and δ, respectively. The coefficient of variation measures the percentage scatter in the observations about the mean and thus is a readily understandable way to express the precision of the observations.

The modified experimental plan for this test called for 22 *runs*. On each run, the collaborative teams were expected to collect simultaneous samples from the stack in accordance with Method 7. Since the actual NO_x emission concentration in the stack fluctuates, one can in general expect different true concentrations for each run. To permit a complete statistical analysis, the individual runs are

grouped into *blocks*, where each block has approximately the same true emission concentration level.

We can apply the statistical terms of the preceding paragraphs both to the collaborators' values during a given run and to each collaborator's values in a given block. In this report, statistical results from the first situation are referred to as *run results*. Those from the second situation are referred to as *collaborator block results*. For example, a run mean is the average of each collaborator's concentration level for the run as obtained by Method 7. A collaborator block coefficient of variation is the ratio of the unbiased standard deviation estimate to the sample mean for all of a collaborator's runs grouped in the block.

The variability associated with a Method 7 concentration determination is estimated in terms of the *within-laboratory* and the *between-laboratory precision components*. In addition, a *laboratory bias component* can be estimated. The following definitions of these terms are given with respect to a *true stack concentration*, μ:

- *Within-laboratory*—The within-laboratory standard deviation, σ, measures the *dispersion in replicate single determinations* made using Method 7 by one laboratory team (same field operators, laboratory analyst, and equipment) sampling the same true concentration, μ. The value of σ is estimated from within each collaborator block combination.

- *Between-laboratory*—The between-laboratory standard deviation, σ_b, measures the *total variability in a concentration determination* due to simultaneous Method 7 determinations by different laboratories sampling the same true stack concentration, μ. The between laboratory variance, σ_b^2, may be expressed as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

  and consists of a within-laboratory variance plus a *laboratory bias variance*, σ_L^2. The between-laboratory standard deviation is estimated using the run results.

- *Laboratory bias*—The laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, is that portion of the total variability that can be ascribed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in the method. This term measures that part of the total variability in a determination which results from the use of the method by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

B. The Collaborative Test Plan

The collaborative test plan called for samples to be drawn on four successive days by four collaborative teams sampling simultaneously. The samples were to be taken through the four sample

ports described in Section II, and these were arbitrarily assigned the labels A, B, C, and D. Due to the plant problems discussed earlier, however, the sampling period was shortened to three days.

While the ports are located so as to be as nearly equivalent as possible, the stack flow characteristics can lead to a difference in concentrations dependent upon the port from which the sample was taken. To offset this possibility, the teams rotated and sampled through different ports on each run.

The starting port for each collaborator was chosen by a randomization method, and subsequently each crew rotated in a systematic manner to an adjacent port. While it would be more desirable to re-randomize after each run, the difficulties involved in the movement of equipment and in having four crews operating on a small platform at the same time made this impracticable.

The Mobay plant had a split beam analyzer which monitored the NO_x levels during operation. These values were used as a basis for establishing blocks for the analysis of the data. The values are presented in Table B1.

During the second day and the third day of sampling, the level reported by the on-stream analyzer remained essentially constant. Each of these days, then, was used as a block of size 8. The data from the first day's run were not homogeneous with respect to concentration level, but these values were taken to be a block since other conditions were comparable throughout. The data were then adjusted for a common mean level with regard to the on-stream analyzer, and these adjusted values were used to obtain collaborator block variability estimates. The result, then, was 22 runs divided among three blocks where each day of samples constituted a block. The blocks were of size 6, 8, and 8, respectively.

In addition to the 22 samples taken from the stack, samples were taken from standard gas mixtures at the Southwest Research Institute Laboratory. Three samples were obtained by each collaborator at each of three levels of NO_x concentration, under conditions which closely mirrored those under which the stack samples were drawn. These standards were prepared and verified by personnel from the National Bureau of Standards, and were used to obtain a measure of the accuracy of Method 7 at varying concentration levels.

To estimate the amount of variation in a test result due to the analytical procedure, three standard solutions were prepared. The collaborators were instructed to analyze these in three replicates on each of three days during which the test samples were being analyzed. A copy of the instruction and reporting form is shown in Figure 5. These results should contain no variation except that due to the laboratory work necessary to determine the concentration level.

C. The Collaborative Test Data

The collaborative test data upon which the analysis was based are shown in Table 1. These values represent the concentrations reported by the collaborators as verified by preliminary calculation checks and, in some cases, recalculated to correct errors in the reported values. In Appendix B.1, the originally reported data are shown and the rationale behind the recalculation explained.

A series of nitrate solutions are provided to each collaborator. These solutions are labeled A, B, and C, and the concentrations are unknown to the collaborators.

Each unknown solution is to be analyzed in triplicate on each of three separate days. Use a 10 ml aliquot and follow the procedure in Section 5.2 (and 4.3) of Method 7 and report results as micrograms of NO_2 per ml of unknown solution.

Submit the results on this sheet along with your other collaborative test data.

Analyst_____

		Concentration, µg NO_2 per ml		
Day	Replicate	Solution A	Solution B	Solution C
Day 1 Date_____	1			
	2			
	3			
Day 2 Date_____	1			
	2			
	3			
Day 3 Date_____	1			
	2			
	3			

FIGURE 5. COLLABORATIVE TEST OF METHOD 7, INSTRUCTIONS FOR ANALYSIS OF UNKNOWN NITRATE SOLUTIONS

TABLE 1. CORRECTED NITROGEN OXIDES COLLABORATIVE TEST DATA, NO_x AS NO_2 (DRY BASIS), lbs/scf × 10^7

Block	Run	Lab 101		Lab 102		Lab 103		Lab 104	
		Data	Port	Data	Port	Data	Port	Data	Port
1	1	335	A	337	B	257	C	203	D
	2	448	B	344	C	330	D	410	A
	3	254	C	306	D	394	A	391	B
	4	329	D	305	A	217	B	279	C
	5	251	A	166	B	188	C	255	D
	6	203	B	63	C	187	D	230	A
2	7	105	C	102	D	97	A	45*	B
	8	112	D	333*	A	89	B	98	C
	9	112	A	104	B	86	C	93	D
	10	108	B	103	C	91	D	111	A
	11	107	C	62	D	98	A	107	B
	12	107	D	89	A	94	B	108	C
	13	93	A	98	B	101	C	96	D
	14	112	B	102	C	96	D	103	A
3	15	119	D	2†	A	89	B	85	C
	16	115	C	3†	D	100	A	76	B
	17	120	B	3†	C	94	D	84	A
	18	144	A	3†	B	94	C	97	D
	19	127	D	3†	A	101	B	95	C
	20	133	C	2†	D	121	A	87	B
	21	120	B	2†	C	98	D	87	A
	22	163	A	3†	B	98	C	113	D

*Values eliminated from the analysis as outliers.
†Values regarded as missing due to analyst error.

Note: EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report, the factor is:

$$10^{-7}\ \text{lb/scf} = 1.6018 \times 10^{3}\ \mu\text{g/m}^3$$

The values for lab 102 in block 3 were treated as missing values, due to failure of the analyst to neutralize the samples prior to evaporization to dryness, with resultant loss of the nitrogen containing species as HNO_3. The values of lab 102 in run 8 and lab 104 in run 7 were omitted from the analysis as erroneous values due to the magnitude of the difference between these values and the other collaborators for those runs, following an outlier test as shown in Appendix B.1.

In these cases, no attempt is made to substitute for these values in the analysis. Rather than this, it is better to work only with those values which are the direct result of a Method 7 test. Substituted values generally tend to minimize the effect of the substitution on the error terms, but by so doing may inordinately decrease the estimate. Thus it is preferable to operate with the missing results when the size of the test permits.

In Appendix B.2, the hypothesis of no port effect is tested. This test is performed according to Youden's[5] rank test at the 5% level of significance. Differences among the sample values due to the port from which the sample was taken are not found to be significant. As a result, no allowance for a port factor is included in the subsequent analyses.

D. The Accuracy of Method 7

In order to ascertain the accuracy of Method 7, samples were drawn from mixtures prepared by personnel from the National Bureau of Standards. Three NO_x concentration levels were used, low, medium, and high, and these levels were generated by mixing a known amount of 0.98 mole percent NO in N_2 mixture into a controlled air flow. The samples were drawn into an evacuated flask, and these were then analyzed according to Method 7.

The values obtained by the collaborators are presented in Table 2, with values for lab 102 in repetition 3 for the medium concentration and lab 103 in repetition 3 for the high concentration not reported due to analyst error. The actual concentration levels for the samples were verified by NBS after the test, and these are also shown.

TABLE 2. NITROGEN OXIDE EMISSIONS FROM NBS SAMPLES
(Parts Per Million)

Level	Repetition	Labs			
		101	102	103	104
107	1	112	131	109	118
	2	120	115	90	115
	3	124	139	99	104
344	1	341	344	325	365
	2	341	350	408	385
	3	341	–	343	347
784	1	637	802	823	769
	2	661	817	768	785
	3	597	764	–	737

TABLE 3. CONFIDENCE INTERVALS FOR GAS SAMPLE MEANS

Concentration, ppm	Mean	St. Dev.	St. Error	t	CI_{95}
107	115	13	4	2.201	106-123
344	354	24	7	2.228	338-370
784	742	76	21	2.228	695-789

Confidence intervals around the sample mean for each concentration across the collaborators are used to determine the accuracy of the NO_x concentrations obtained. Values of the pertinent statistics are given in Table 3. *The method may be said to be accurate at each level if the actual concentration lies within the 95% confidence interval around the sample mean.*

For each of the concentrations, the true value does lie in the confidence interval, falling in the low range for the 107 ppm and 344 ppm values, and in the high range for the 784 ppm value. From this, then, we can conclude that in all three ranges, low, medium, and high, the method does provide an accurate estimate of the true concentration level. However, there is considerable scatter among the observations at the higher concentrations, as reflected by their standard deviations.

E. The Precision of Method 7

Of prime importance in the evaluation of Method 7 is the estimation of the precision that is associated with the determination of NO_x concentrations. This precision is estimated in terms of between-laboratory and within-laboratory standard deviations, as previously defined.

In analyzing the data, the first consideration is to determine, if possible, the distributional nature of the reported concentrations. To accomplish this, the concentrations are transformed using two common variance-stabilizing transformations, the logarithmic and the square root, and the degree of equality of variance obtained is determined. In addition, the untransformed data are also tested, and the three forms are compared in Appendix B.3. For the run data, the logarithmic transformation produces the best results and is accepted as the most likely model for the data. This acceptance implies that there is a proportional relationship between the true mean and standard deviation.[3]

To further this argument, the sample mean and standard deviation are examined by means of a regression through the origin to see if the theoretical relationship proposed seems valid on an empirical basis. The details are provided in Appendix B.4, and the least squares fit and the individual points are shown in Figure B.1.

The paired sample means and standard deviations exhibit an apparent linear trend, and an investigation of the correlation terms confirms this. The coefficient of correlation for these values is 0.936 which is a significant value at the 5 percent level of significance. The coefficient of determination for the no intercept model is 0.876, indicating that 87.6 percent of the change in magnitude of the standard deviation is due to a change in the magnitude of the mean.

A similar analysis is used on the collaborator block mean and standard deviation, again using a regression through the origin. The line which provides the least squares fit through the origin is shown in Figure B.2. The value of the coefficient of correlation is 0.907 which also is significant at the 5 percent level. This gives a coefficient of determination for the collaborator block data of 0.823.

Thus, on both a theoretical and an empirical basis, we can say that the mean and standard deviation for the run data are proportional to one another. In terms of the between-laboratory standard deviation, σ_b, for the true determination mean, δ,

$$\sigma_b = \beta_b \delta,$$

where β_b is the true between-laboratory coefficient of variation. For the collaborator block data, on an empirical basis, we can also say that there is a proportionality between the mean and standard deviation. In terms of the within-laboratory component, σ, and the true mean determination, δ,

$$\sigma = \beta\delta$$

where β is the true within-laboratory coefficient of variation.

Thus, we can obtain estimates of σ and σ_b by estimating the proportionality factors, or coefficients of variation, and expressing the estimates as percentages of the true mean determination. In Appendix B.5 the technique for obtaining best estimates of the coefficients of variation is discussed, and it is demonstrated that the resulting estimates are unbiased for the standard deviations of interest. We refer to these estimates as $\hat{\sigma}$ and $\hat{\sigma}_b$, and express them as

$$\hat{\sigma} = \hat{\beta}\delta$$

and

$$\hat{\sigma}_b = \hat{\beta}_b \delta,$$

where $\hat{\beta}$ and $\hat{\beta}_b$ are the estimated coefficients of variation, and δ represents the true mean of the determinations.

In Appendix B.6, the estimates of β and β_b are obtained. The within-laboratory coefficient of variation is $\hat{\beta} = (0.1488)$, which gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = (0.1488)\delta$$

with 67 degrees of freedom.

Similarly, we obtain from the run data, $\hat{\beta}_b = (0.1847)$, which gives an estimated between-laboratory standard deviation of

$$\hat{\sigma}_b = (0.1847)\delta,$$

with 3 degrees of freedom.

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_b^2 - \hat{\sigma}^2}$$

$$= \sqrt{(0.1847)^2\delta^2 - (0.1488)^2\delta^2}$$

$$\hat{\sigma}_L = \delta\sqrt{(0.1847)^2 - (0.1488)^2}$$

$$= (0.1094)\delta.$$

F. The Accuracy and Precision of the Analytical Procedure

As previously discussed, the collaborators were given three standard nitrate solutions for analysis in conjunction with the collaborative test samples. The actual concentration was unknown to the collaborators, and this gave a basis for determining accuracy and precision for the lab procedure alone.

The true concentration for solutions A, B, and C were 38.2, 7.2, and 22.3 μg/mℓ, respectivelv. The test for accuracy was as for the gas samples in section III, D, by constructing confidence intervals around the sample mean values. The *mean* is the average of the nine individual determinations for all four collaborators taken together and thus has an *estimated variance* of $\hat{\sigma}_L^2/4 + \hat{\sigma}^2/36$. Using the values in Appendix B.8 for each solution of MS_L and σ^2_r, we obtain the *confidence intervals* shown in Table 4.

TABLE 4. ACCURACY OF THE ANALYTICAL PROCEDURE

Solution	True Concentration μg NO_3/mℓ	Sample Mean μg NO_3/mℓ	Confidence Interval
A	38.2	37.94	$33.26 < \mu < 42.62$
B	7.2	6.00	$4.25 < \mu < 7.75$
C	22.3	22.21	$19.84 < \mu < 24.59$

For each level of concentration, the overall mean estimates are shown to be accurate at the 5% level of significance, based on 36 individual determinations. In all cases, in fact, the true mean is well within the interval obtained, although in all cases there is a tendency of the sample mean to be below the true value.

The *precision estimates* obtained are shown in Table B.12 for the analytical procedure alone. For the within-laboratory component, $\hat{\sigma}_r^2$, no dependency on the value of the mean could be detected. Thus, the best estimate of this value that we can obtain for the analytical portion of the method is the average of the three values. This gives

$$\hat{\sigma}^2 = \frac{1}{3}\,[0.8094 + 2.5664 + 0.9381]$$

$$= 1.438$$

and

$$\hat{\sigma} = \sqrt{1.43797}$$

$$= 1.199.$$

The *laboratory bias component*, σ_L, tends to rise as the concentration rises, so that a regression technique is used as the best estimate for σ_L. Using the true concentration means and the values of $\hat{\sigma}_L$, we obtain

$$\hat{\sigma}_L = 0.725 + (0.092)\mu$$

where μ represents the true concentration level.

From these results, it appears that as the concentration rises, the *total variability* in the analytical phase becomes more and more a function of the laboratory bias variance component.

The principal cause of differences among labs is shown in Appendix B.8 to be the day-to-day variations in lab procedures. This is likely a result of drift in the spectrophotometer absorbance readings. It was noted that the collaborators tended to use a single absorbance curve for all the concentrations from the stack samples, the gas samples, and the standard solutions. With these results, and those in the earlier study by Hamil and Camann,[3] it appears that daily recalibration is necessary to reduce this lab bias component.

The investigation of the precision estimates obtained from the nitrate solution data revealed no significant tendency of the within-laboratory components to rise as the concentration rises. This negates the coefficient of variation approach. However, for each solution studied, the lab bias of the analytical procedure is the primary contributor to the total variation. This suggests that if improvements in the method are to be made, the analytical procedures are the most likely areas for revising or making additional stipulations to the procedure.

IV. COMPARISONS WITH PREVIOUS STUDY

The following comparisons can be made to the results obtained by Hamil and Camann in the previous study on Method 7.[3]

The distributional characteristics of the data were essentially the same. In both cases, the logarithmic transformation proved to be marginally acceptable, while the linear and square root transforms did not perform as well. In both cases, a linear dependency was established between mean and standard deviation for the collaborative test data.

The accuracy tests conducted with the previous test proved to be inconclusive due to problems resulting from the absence of oxygen in the gas standards but indicated that a reasonable amount of accuracy could be expected. In following the recommendation that further accuracy tests be conducted, the results of this study show that at all levels studied the method provides accurate estimates of the true concentration levels, using a 5 percent level of significance.

Both the within-laboratory and between-laboratory standard deviation estimates were greater in this report than in the previous one, but this was in large measure attributable to the contribution of the first six runs. Because of this, and the fact that more observations were used to obtain the estimates in the previous study, the true values are probably closer to those obtained by Hamil and Camann.

For the analysis of the unknown nitrate solutions, the only consistently significant factor was the day within collaborator effect. This corresponds to the analysis done on data from four solutions in the power plant study. The variance components for these data could not be justified as suitable for a coefficient of variation approach, and the within-lab component, $\hat{o}^2$, was independent of the concentration level.

V. RECOMMENDATIONS

The following assessments of and recommendations on Method 7 have been made as a result of the preceding results and comparisons.

(1) The calculation errors involved in a Method 7 determination and the varying number of significant digits carried are a major problem area in evaluating the performance of the method. To prevent these from unfairly influencing a performance test for compliance, a standard computer program should be written for EPA to evaluate the test results based on the raw data only. This recommendation has been previously made to EPA.

(2) In utilizing a calibration curve to translate absorbance into mass for determination of a Method 7 result, the techniques vary from lab to lab. By establishing a standardized technique where a least squares line through the origin is generated, then the slope used to calculate the mass, the results will be more self-consistent and reliable. The use of lines drawn freehand and the inaccuracies involved in reading values from a graph lead to variations in the reported values that need not be there. At least three significant digits should be maintained when calculating the slope of the line.

(3) The day-to-day variations in lab procedure contributed significantly to the variation in the analytical portion of the test. A requirement should be made that the spectrophotometer be recalibrated daily and a new calibration line drawn. This should somewhat negate the effect of the drift on the determinations.

(4) Due to the many handling steps and chance for mishap, it is strongly recommended that an aliquoting section be inserted into the procedure. Aliquoting of samples is a basic procedure in analytical chemistry and would help in the determination of precision in the results. It would also guard against the loss of sample and data if mishap occurs in analysis, as occurred in the analyses of these samples.

Enactment of these recommendations could greatly enhance the precision of Method 7 and facilitate the use of the method in obtaining NO_x concentrations.

APPENDIX A

METHOD 7. DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

Federal Register, Vol. 36, No. 247
December 23, 1971

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METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measure colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling. See Figure 7-1.

2.1.1 Probe—Pyrex[1] glass, heated, with filter to remove particulate matter. Heating is unnecessary if the probe remains dry during the purging period.

2.1.2 Collection flask—Two-liter, Pyrex,[1] round bottom with short neck and 24/40 standard taper opening, protected against implosion or breakage.

[1] Trade name.

2.1.3 Flask valve—T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature gauge—Dial-type thermometer, or equivalent, capable of measuring 2° F. intervals from 25° to 125° F.

2.1.5 Vacuum line—Tubing capable of withstanding a vacuum of 3 inches Hg absolute pressure, with "T" connection and T-bore stopcock, or equivalent.

2.1.6 Pressure gauge—U-tube manometer, 36 inches, with 0.1-inch divisions, or equivalent.

2.1.7 Pump—Capable of producing a vacuum of 3 inches Hg absolute pressure.

2.1.8 Squeeze bulb—One way.

2.2 Sample recovery.

2.2.1 Pipette or dropper.

2.2.2 Glass storage containers—Cushioned for shipping.

2.2.3 Glass wash bottle.

2.3 Analysis.

2.3.1 Steam bath.

2.3.2 Beakers or casseroles—250 ml., one for each sample and standard (blank).

2.3.3 Volumetric pipettes—1, 2, and 10 ml.

2.3.4 Transfer pipette—10 ml. with 0.1 ml. divisions.

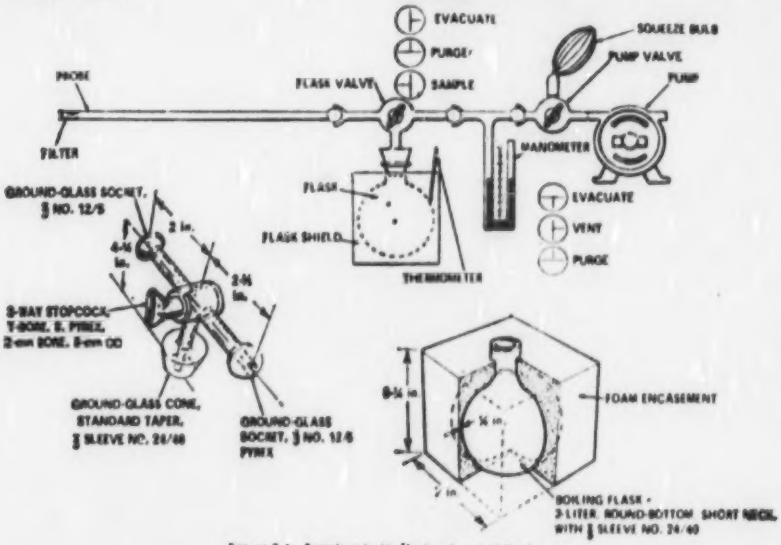

Figure 7-1. Sampling train, flask valve, and flask.

2.3.5 Volumetric flask—100 ml., one for each sample, and 1,000 ml. for the standard (blank).

2.3.6 Spectrophotometer—To measure absorbance at 420 nm.

2.3.7 Graduated cylinder—100 ml. with 1.0 ml. divisions.

2.3.8 Analytical balance—To measure to 0.1 mg.

3. *Reagents.*

3.1 Sampling.

3.1.1 Absorbing solution—Add 2.8 ml. of concentrated H_2SO_4 to 1 liter of distilled water. Mix well and add 6 ml. of 3 percent hydrogen peroxide. Prepare a fresh solution weekly and do not expose to extreme heat or direct sunlight.

3.2 Sample recovery.

3.2.1 Sodium hydroxide (1*N*)—Dissolve 40 g. NaOH in distilled water and dilute to 1 liter.

3.2.2 Red litmus paper.

3.2.3 Water—Deionized, distilled.

3.3 Analysis.

3.3.1 Fuming sulfuric acid—15 to 18% by weight free sulfur trioxide.

3.3.2 Phenol—White solid reagent grade.

3.3.3 Sulfuric acid—Concentrated reagent grade.

3.3.4 Standard solution—Dissolve 0.5495 g. potassium nitrate (KNO_3) in distilled water and dilute to 1 liter. For the working standard solution, dilute 10 ml. of the resulting solution to 100 ml. with distilled water. One ml. of the working standard solution is equivalent to 25 μg. nitrogen dioxide.

3.3.5 Water—Deionized, distilled.

3.3.6 Phenoldisulfonic acid solution—Dissolve 25 g. of pure white phenol in 150 ml. concentrated sulfuric acid on a steam bath. Cool, add 75 ml. fuming sulfuric acid, and heat at 100° C. for 2 hours. Store in a dark, stoppered bottle.

4. *Procedure.*

4.1 Sampling.

4.1.1 Pipette 25 ml. of absorbing solution into a sample flask. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to at least 3 inches Hg absolute pressure. Turn the pump valve to its "vent" position and turn off the pump. Check the manometer for any fluctuation in the mercury level. If there is a visible change over the span of one minute, check for leaks. Record the initial volume, temperature, and barometric pressure. Turn the flask valve to its "purge" position, and then do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its "vent" position. Turn the flask valve to its "sample" position and allow sample to enter the flask for about 15 seconds. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for 5 minutes.

4.2 Sample recovery.

4.2.1 Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer, open the valve from the flask to the manometer, and record the flask pressure and temperature along with the barometric pressure. Transfer the flask contents to a container for shipment or to a 250 ml. beaker for analysis. Rinse the flask with two portions of distilled water (approximately 10 ml.) and add rinse water to the sample. For a blank use 25 ml. of absorbing solution and the same volume of distilled water as used in rinsing the flask. Prior to shipping or analysis, add sodium hydroxide (1*N*) dropwise into both the sample and the blank until alkaline to litmus paper (about 25 to 35 drops in each).

4.3 Analysis.

4.3.1 If the sample has been shipped in a container, transfer the contents to a 250 ml. beaker using a small amount of distilled water. Evaporate the solution to dryness on a steam bath and then cool. Add 2 ml. phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a glass rod. Make sure the solution contacts all the residue. Add 1 ml. distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Cool, add 20 ml. distilled water, mix well by stirring, and add concentrated ammonium hydroxide dropwise with constant stirring until alkaline to litmus paper. Transfer the solution to a 100 ml. volumetric flask and wash the beaker three times with 4 to 5 ml. portions of distilled water. Dilute to the mark and mix thoroughly. If the sample contains solids, transfer a portion of the solution to a clean, dry centrifuge tube, and centrifuge, or filter a portion of the solution. Measure the absorbance of each sample at 420 nm. using the blank solution as a zero. Dilute the sample and the blank with a suitable amount of distilled water if absorbance falls outside the range of calibration.

5. *Calibration.*

5.1 Flask volume. Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to ±10 ml. Number and record the volume on the flask.

5.2 Spectrophotometer. Add 0.0 to 16.0 ml. of standard solution to a series of beakers. To each beaker add 25 ml. of absorbing solution and add sodium hydroxide (1*N*) dropwise until alkaline to litmus paper (about 25 to 35 drops). Follow the analysis procedure of section 4.3 to collect enough data to draw a calibration curve of concentration in μg. NO_2 per sample versus absorbance.

6. *Calculations.*

6.1 Sample volume.

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$$V_{sc} = \frac{T_{std}(V_f - V_s)}{P_{std}}\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = \left(17.71\ \frac{°R}{\text{in. Hg}}\right)(V_f - 25\ \text{ml.})\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right)$$ Equation 7-1

where:

V_{sc} = Sample volume at standard conditions (dry basis), ml.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Pressure at standard conditions, 29.92 inches Hg.

V_f = Volume of flask and valve, ml.

V_s = Volume of absorbing solution, 25 ml.

P_f = Final absolute pressure of flask, inches Hg.

P_i = Initial absolute pressure of flask, inches Hg.

T_f = Final absolute temperature of flask, °R.

T_i = Initial absolute temperature of flask, °R.

6.2 Sample concentration. Read μg. NO_2 for each sample from the plot of μg. NO_2 versus absorbance.

$$C = \left(\frac{m}{V_{sc}}\right)\left(\frac{1\ \text{lb.}}{1.6\times10^{9}\ \frac{\mu\text{g.}}{\text{ml.}}\ \text{cu. ft.}}\right) = \left(6.2\times10^{-5}\ \frac{\text{lb./s.c.f.}}{\mu\text{g./ml.}}\right)\left(\frac{m}{V_{sc}}\right)$$ equation 7-2

where:

C = Concentration of NO_2 as NO_2 (dry basis), lb./s.c.f.

m = Mass of NO_2 in gas sample, μg.

V_{sc} = Sample volume at standard conditions (dry basis), ml.

7. *References.*

Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc., 1962, vol. 1, p. 329–330.

Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure), In: 1968 Book of ASTM Standards, Part 23, Philadelphia, Pa. 1968, ASTM Designation D–1608–60, p. 726–729.

Jacob, M. B., The Chemical Analysis of Air Pollutants, New York, N.Y., Interscience Publishers, Inc., 1960, vol. 10, p. 351–356.

APPENDIX B. STATISTICAL METHODS

This appendix consists of various sections which contain detailed statistical procedures carried out in the analysis of the NO_x collaborative study data. Reference to these sections has been made at various junctures in the Statistical Design and Analysis part of the body of this report. Each Appendix B section is an independent ad hoc statistical analysis pertinent to a particular problem addressed in the body of the report.

TABLE B.1. ORIGINAL COLLABORATIVE TEST DATA, NO_x AS NO_2, lb/scf X 10^7

Run	Lab 101	Lab 102	Lab 103	Lab 104	On-Stream Analyzer
1	328	377	210	302	237
2	444	344	280	409	260
3	247	306	330	391	266
4	328	305	180	279	207
5	258	166	160	255	172
6	209	14	150	230	154
7	105	102	80	43	77
8	111	333	70	98	77
9	111	104	70	93	77
10	108	102	70	111	77
11	106	62	80	108	77
12	107	89	80	108	83
13	92	98	80	96	83
14	111	102	80	103	83
15	118	2	80	86	80
16	116	4	90	76	83
17	118	4	80	83	89
18	142	4	80	97	89
19	128	4	90	95	89
20	134	2	110	87	89
21	119	2	80	87	89
22	160	4	80	113	118

B.1 Preliminary Analysis of the Original Collaborative Test Data

In order to insure that the results obtained from the Method 7 test at the Mobay site were indicative of the performance of the method itself, preliminary recalculation of the data was performed. This serves to verify that the collaborators had calculated their concentration levels using the proper formulas and conversion factors. In addition, when a particular laboratory showed a consistent bias, possible causes were investigated both by examining the collaborator work sheets and by contacting that laboratory concerning their procedure. The data as were originally reported appear in Table B.1, and the verified or corrected data as used in the analysis appear in Table 1.

The values of lab 102 in runs 15-22 were eliminated from the analysis. The actual concentrations determined were treated as lost values, due to the probable omission of the neutralization step in the analytical procedure, which resulted in the loss of the nitrogen containing species as HNO_3 upon evaporation of the samples to dryness.

The reported values of lab 103 were almost uniformly lower than those by the other collaborators, and possible causes for this were investigated by inspecting the work sheets provided. Lab 103 has set up an absorbance curve using five reference points. The line to match these points had been drawn in such a manner as to pass nearly through three points and to essentially ignore the effect of the other two. The two points that did not contribute to the slope of the line, however, were above the line, and their inclusion would have the effect of increasing the slope and raising all the values. A new curve was constructed using a least squares fit to these points through the origin. The slope of this line times the absorbance provides the mass of each sample. It should be stressed that although an adjustment of the data was made, it was made using the actual information obtained by the collaborators and in this light seems a valid procedure.

The values from lab 102 in run 8, and lab 104 in run 7 were regarded as suspicious due to the magnitude of the difference between those values and both the on-stream analyzer and the values reported by the other collaborators during that run. Using a test for outlying values given in Dixon and Massey[1], these values may be excluded from the analysis. The test is based on the ratio of

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the difference between the suspect value and its closest value to the entire range of the sample. For run 7, this becomes, using the corrected values from Table 1,

$$r = \frac{97 - 45}{105 - 45} = \frac{52}{60} = 0.867,$$

and for run 8,

$$r = \frac{333 - 112}{333 - 89} = \frac{221}{244} = 0.906.$$

These values may be said to be outlying if r exceeds the tabled value for four observations at the 95 percent level of confidence. From a table given in[1], the critical value of r is 0.765, and thus both values are rejected as outliers.

In these cases, there is no substitution for these values, but the analysis is done on the remaining values only. In this manner, the final estimates are obtained only from actual Method 7 determinations, made in accordance with the *Federal Register*.[2]

During the first six runs, the values read from the on-stream analyzer were fluctuating considerably. This was due to the fact that a rupture disc blew, causing the plant to have to begin shutdown during the first day of the test. To obtain collaborator block variance estimates from these values, it was necessary to make a compensating adjustment for the fluctuating mean value.

The value of the fourth run on day 1 on the on-stream analyzer of 207 appeared to be a good central point of the first day's values. The adjustment used was to make a correction in the data for the difference between the on-stream analyzer at that point and the value of 207. In this manner, the differences between collaborators are maintained, while the block estimates are adjusted to a common mean value. The values of the first six runs adjusted for a mean of 207 are presented in Table B.2, and the collaborator block values are taken from these. For between-collaborator estimates, the original data are used, as they appear in Table 1.

TABLE B.2. CORRECTED VALUES FOR BLOCK 1, ADJUSTED FOR COMMON MEAN

Run	Lab 101	Lab 102	Lab 103	Lab 104
1	293	330	225	177
2	356	274	263	326
3	198	238	306	304
4	329	305	217	279
5	303	200	227	308
6	273	85	252	309

B.2 Significance of the Port Effect

The sampling at the Mobay site was done through four sample ports, assigned the labels A, B, C, and D. Each collaborator sampled from only one port during each run, and although the ports are as nearly identical as possible, the pattern of the gas flow may lead to one port showing a consistently higher or consistently lower concentration than the others.

To test this possibility, a *rank test* proposed by Youden[5] is used on the data. Each port is assigned a rank during each run, based on the reported concentration, one being the highest ranking concentration. These ranks are then summed for each port, and the values compared to the limits of a *95% confidence interval* tabled by Youden.

Table B.3 shows the details of the test. For the missing values of lab 103, the port was assigned the lowest rank. This involved two observations from each data port, and it was felt that the effect would be to maintain the relationship between the three good port observations.

TABLE B.3. TEST FOR PORT EFFECT

Run	Port Ranks			
	A	B	C	D
1	2	1	3	4
2	2	1	3	4
3	1	2	4	3
4	2	4	3	1
5	2	4	3	1
6	1	2	4	3
7	3	4	1	2
8	1	4	3	2
9	1	2	4	3
10	1	2	3	4
11	3	1.5	1.5	4
12	4	3	1	2
13	4	2	1	3
14	2	1	3	4
15	4	2	3	1
16	2	3	1	4
17	3	1	4	2
18	1	4	3	2
19	4	2	3	1
20	2	3	1	4
21	3	1	4	2
22	1	4	3	2
Rank Sum	49	53.5	59.5	58

Youden's Confidence Interval: 4 ports, 22 runs, (40, 70)
H_O: No port effect. H_A: (not H_O)
Reject H_O if and only if a Rank Sum falls outside CI.
Conclusion: Accept H_O, no significant port effect.

The highest port rank sum for the Mobay site was for port C, with a value of 59.5, and the low was port A, with a value of 49. The extreme values at a 5 percent significance level for the test are 40 and 70, and thus the values obtained are acceptable. No differences in reported NO_x concentration due to the port from which the sample was taken are detectable, and as a result, the port factor is not included in any further analysis.

B.3 Transformations

Transformations are applied to the test data for two purposes. First, it can put the data into an acceptable form for performing an analysis of variance. Secondly, it can provide a clue to the true nature of the distribution of the sample data and thus provide a model for the interpretation of the data.

The concentrations are analyzed under two common variance stabilizing transformations and in their original (linear) form. For each, *Bartlett's test for homogeneity of variance*[1] is used to determine the adequacy of the two transformations and the degree of equality of variance present in the original data. The transformations used were the *logarithmic* and the *square root*. The results obtained for Bartlett's test are shown in Table B.4.

The test statistic is based on the *chi-square distribution* and the corresponding significance level is the probability of obtaining a chi-square value at least that great due to chance alone. Clearly the logarithmic transformation provides the best fit to the data, even though this would be only marginally acceptable. These results are consistent with those presented by Hamil and Camann[3] in their study on Method 7.

This acceptance of a logarithmic transformation as the most suitable model for the test data indicates that a *linear relationship* exists between the true mean and the true standard deviation for the run data. A proof of this is presented by Hamil and Camann.[3]

TABLE B.4. DATA TRANSFORMATION TO ACHIEVE RUN EQUALITY OF VARIANCE

Transformation	Test Statistic	DF	Significance Level
Linear	57.980	21	<0.01
Logarithmic	36.458	21	0.02
Square Root	41.443	21	0.01

B.4 Empirical Relationship Between the Mean and Standard Deviation in the Collaborative Test Data

In order to properly analyze the data, it is necessary to determine any underlying relationship between the mean and standard deviation. We wish to do this for both the interlaboratory run component and the intralaboratory collaborator block component on an empirical basis.

Let us denote,

x_{ijk} as the concentration reported by i in block j during run k

$\bar{x}_{.jk} = \frac{1}{p}\sum_{i=1}^{p} x_{ijk}$, as the mean for run k in block j, where p is the number of collaborators.

$s_{jk} = \sqrt{\frac{1}{p-1}\sum_{i=1}^{p}(x_{ijk} - \bar{x}_{.jk})^2}$, as the standard deviation for run k, block j.

The values obtained for $x_{.jk}$ and s_{jk} for each of the 22 runs are presented in Table B.5, along with the coefficients of variation for each run. Asterisks denote those runs in which only three collaborators values were used in the calculations.

TABLE B.5. INTERLABORATORY RUN SUMMARY

Block	Run	NO_x as NO_2 (lb/scf) x 10^{+7}		Coefficient of Variation
		$\bar{x}_{.jk}$	s_{jk}	
1	1	283.0	65.1	0.2299
	2	383.0	55.6	0.1452
	3	336.2	68.3	0.2033
	4	282.5	48.2	0.1706
	5	215.0	44.8	0.2085
	6	170.7	74.0	0.4333
2	*7	101.3	4.0	0.0399
	*8	99.7	11.6	0.1163
	9	98.8	11.5	0.1167
	10	103.2	8.8	0.0853
	11	93.5	21.4	0.2291
	12	99.5	9.5	0.0952
	13	97.0	3.4	0.0347
	14	103.2	6.6	0.0639
3	*15	97.7	18.6	0.1903
	*16	97.0	19.7	0.2028
	*17	99.3	18.6	0.1871
	*18	111.7	28.0	0.2511
	*19	107.7	17.0	0.1580
	*20	113.7	23.9	0.2099
	*21	101.7	16.8	0.1653
	*22	124.7	34.0	0.2730

*Values obtained using 3 determinations.

There is an apparent linear relationship between the run mean and standard deviation, and to test this idea, a standard *least squares regression line* is fitted to the observed values. A *no intercept model* is used, to include the origin (mean and standard deviation both equal to zero). The regression line thus generated and the individual points used are presented in Figure B.1.

As a measure of the validity of the model, a correlation coefficient, r, and coefficient of determination, r^2, are computed for the data. For the no-intercept model, the correlation coefficient is calculated according to the formula[4]

$$r = \frac{\sum_{i=1}^{n} x_i y_i}{\sqrt{\sum_{i=1}^{n} x_i^2 \sum_{i=1}^{n} y_i^2}}$$

where x_i represents a sample mean, y_i represents the corresponding standard deviation, and n is the number of points used in the analysis.

For the run data, the value of r is 0.936, which is significant at the 5 percent significance level. The value of r^2, then, is $(0.936)^2 = 0.876$, indicating that over 87% of the variance in the means and the standard deviations is related.

A similar analysis can be performed on the collaborator block data. We denote

$\bar{x}_{ij.} = \frac{1}{n}\sum_{k=1}^{n} x_{ijk}$, as the sample mean of collaborator i, block j, where n is the number of samples in the collaborator block.

$s_{ij} = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(x_{ijk} - \bar{x}_{ij.})^2}$, as the sample standard deviation of collaborator i in block j.

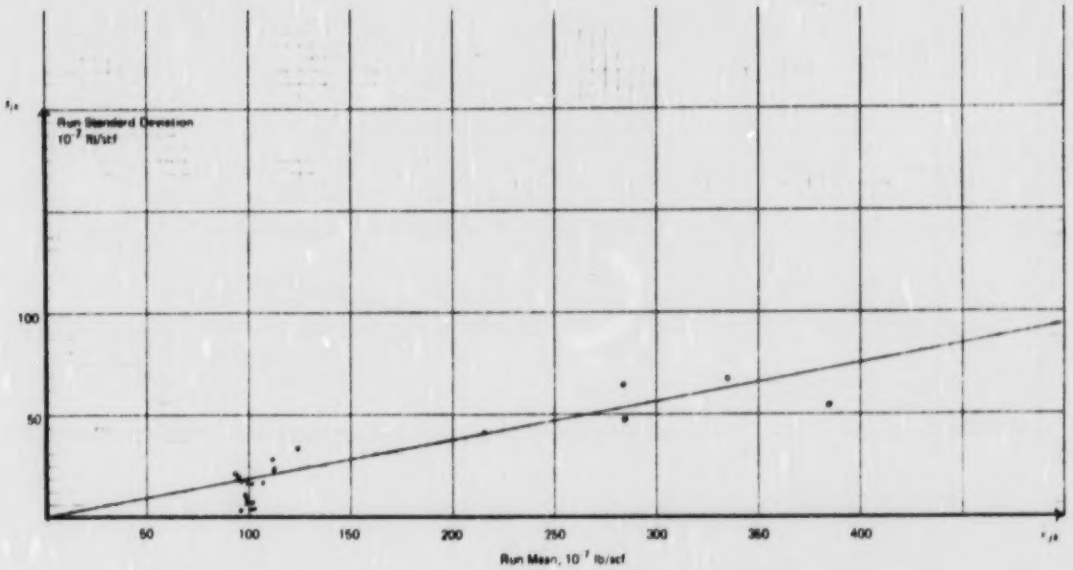

FIGURE B.1. INTERLABORATORY RUN PLOT

The values for the eleven collaborator block combinations are listed in Table B.6. No values are shown for lab 102 in block 3 as no valid concentrations were reported in that group. Values with asterisks were those based on less than the full number of observations for that block.

TABLE B.6. INTRALABORATORY COLLABORATOR BLOCK SUMMARY

Block	Collaborator	NO_X as NO_2 (lb/scf) × 10^{+7}		Coefficient of Variation
		$\bar{x}_{ij.}$	s_{ij}	
1	Lab 101	292.0	54.4	0.1862
	Lab 102	238.7	88.4	0.3705
	Lab 103	248.3	33.3	0.1340
	Lab 104	283.8	54.5	0.1919
2	Lab 101	107.0	6.3	0.0587
	*Lab 102	94.3	15.1	0.1605
	Lab 103	94.0	5.0	0.0533
	*Lab 104	102.3	6.8	0.0662
3	Lab 101	130.1	16.3	0.1249
	Lab 102	–	–	–
	Lab 103	99.4	9.6	0.0962
	Lab 104	90.5	11.2	0.1236

*Collaborator blocks with missing values.

Once again, the standard deviation for the collaborator block data shows an apparent tendency to increase linearly with the mean. The paired means and standard deviations are presented in the graph in Figure B.2. A least squares regression line is determined for these points and is also presented in Figure B.2, to illustrate the degree of fit of the model.

The *correlation coefficient* for the intralaboratory data is 0.907 based on the 11 pairs, $\bar{x}_{ij.}$ and s_{ij}. This value, again, is significant using a 5 percent significance level. The value of r^2 is 0.823, again indicating a high degree of association between the sample mean and sample standard deviation.

B.5 Underlying Relationship Between the Mean and the Standard Deviation

In Appendix B.4, the empirical relationship is established between the mean and standard deviation of the collaborator block data. Let us denote:

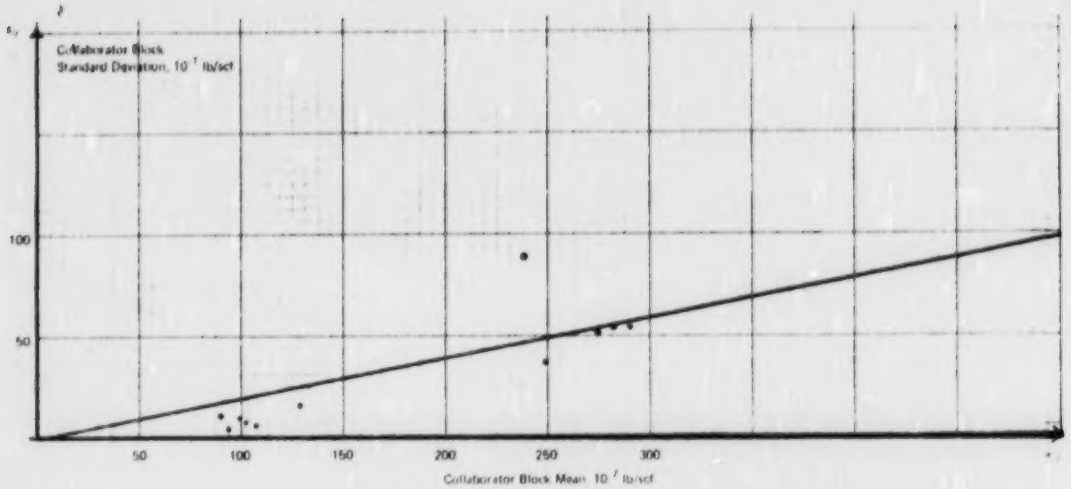

FIGURE B.2. INTRALABORATORY COLLABORATOR BLOCK PLOT

δ, as the true mean of the distribution of the Method 7 determinations

σ, as the true within-lab standard deviation.

and

$\beta = \dfrac{\sigma}{\delta}$ as the true coefficient of variation.

To estimate σ, we use the relationship established in Appendix B.4.

$$s_{ij} = b\bar{x}_{ij}.$$

where b is the sample coefficient of variation. The sample standard deviation is a biased estimator of the population value, but Ziegler[6] has shown that for a sample of size n, this bias may be effectively removed by multiplying by a factor of

$$\alpha_n = \sqrt{\frac{2}{3}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)},$$

where Γ (a) is the standard gamma function. Thus we have

$$\sigma = E(\alpha_n s_{ij})$$

$$= \alpha_n E(s_{ij})$$

and substituting from above,

$$\sigma = \alpha_n E(b\bar{x}_{ij.})$$

$$= \alpha_n b E(\bar{x}_{ij.})$$

$$= \alpha_n b \delta$$

$$= \beta\delta$$

where $\beta = \alpha_n b$.

Similarly, in Appendices B.3 and B.4, the linear relationship between the run mean and run standard deviation is established first on theoretical, then empirical grounds. Thus, we can say that

$$s_{jk} = b'\bar{x}_{.jk}$$

The true between-laboratory standard deviation is given by $\sigma_b = \sqrt{\sigma_L^2 + \sigma^2}$, where σ_L^2 represents the true laboratory bias variance component. As before, s_{jk} is a biased estimator, and the correction factor must be applied. We have

$$\sqrt{\sigma_L^2 + \sigma^2} = E(\alpha_n s_{jk})$$

$$= \alpha_n E(s_{jk})$$

$$= \alpha_n E(b'\bar{x}_{.jk})$$

$$= \alpha_n b' E(\bar{x}_{.jk})$$

$$= \beta_b \delta$$

where $\beta_b = \alpha_n b'$.

From the above relationships, we find

$$\sigma_L^2 + \sigma^2 = \beta_b^2 \delta^2$$

$$\sigma_L^2 = \beta_b^2 \delta^2 - \sigma^2$$

$$= \beta_b^2 \delta^2 - (\beta\delta)^2$$

$$= (\beta_b^2 - \beta^2)\delta^2$$

and this gives us

$$\sigma_L = \sqrt{\beta_b^2 - \beta^2}\,\delta$$

$$= \beta_L \delta$$

where β_L is defined as $\sqrt{\beta_b^2 - \beta^2}$.

B.6 Estimating the Standard Deviation Components

In Appendix B.5, we developed the relationships concerning the standard deviation components for the run and the collaborator block components.

$$\sigma = \beta\delta$$

$$\sigma_L = \beta_L \delta = \sqrt{\beta_b^2 - \beta^2}\,\delta$$

The standard deviation component σ, for the *within-laboratory variability*, and the standard deviation σ_L, for the *laboratory bias* component, both follow the *coefficient of variation hypothesis.* To estimate these standard deviations, we obtain best estimates of the coefficients of variation and express the standard deviations as percentages of the mean value, δ.

From Ziegler[6], the *best estimate* of a coefficient of variation is given by

$$\hat{\beta} = \frac{Cn}{k} \sum_{i=1}^{k} \frac{s_i}{\bar{x}_i}$$

for k samples each of size n. For unequal sample sizes, n_i, this may be extended as

$$\hat{\beta} = \frac{1}{k} \sum_{i=1}^{k} Cn_i \frac{s_i}{\bar{x}_i} ,$$

where Cn_i is the correction factor used to remove the bias on the sample standard deviation.

For the *within-laboratory standard deviation*, σ, this estimate becomes

$$\hat{\beta} = \frac{1}{11} \sum_{i=1}^{3} \sum_{j=1}^{4} Cn_{ij} \frac{\bar{x}_{ij\cdot}}{s_{ij}}$$

where n_{ij} is the number of runs in the collaborator block. The values used are those presented in Table B.6, with the adjusted values in the first block as discussed in Appendix B.1. The *estimated coefficient of variation* is $\hat{\beta}$ = (0.14882) which gives

$$\hat{\sigma} = \hat{\beta}\delta = (0.14882)\delta.$$

Similarly, from the run data we have

$$\hat{\beta}_b = \frac{1}{22} \sum_{j=1}^{3} \sum_{k=1}^{n_j} Cn_{jk} \frac{\bar{x}_{\cdot jk}}{s_{jk}}$$

where n_j is the number of runs in block j, and n_{jk} is the number of collaborator values in block j, run k. For the run data in Table B.5, the estimated $\hat{\beta}_b$ is $\hat{\beta}_b$ = (0.18468) which gives

$$\hat{\sigma}_b = (0.18468)\delta$$

Substituting these values into the second equation, we obtain

$$\hat{\beta}_L = \sqrt{\beta_b^2 - \hat{\beta}^2}$$

$$= \sqrt{(0.03411) - (0.02215)}$$

$$= \sqrt{(0.01196)}$$

$$= 0.10936.$$

Then the estimate for the *lab bias standard deviation* is

$$\hat{\sigma}_L = (0.10936)\delta.$$

B.7 The Nitrate Solution Data

Three nitrate solutions were given to each of the collaborators to be analyzed in conjunction with the collaborative test data. These solutions were analyzed in triplicate on each of three days and give an indication of the effect of the analytical process on the Method 7 concentration determinations. The instruction and reporting form given to the collaborators is shown in Figure 5. The reported concentrations as determined by the lab analysts are shown in Table B.7.

In Table B.8, the values for each solution are averaged for each day for each collaborator. From these, it is evident that fairly large discrepancies do occur in the results obtained by the same lab from day to day. In Table B.9, the average over all three days for each solution is shown.

There is no apparent tendency in the solution averages toward a single laboratory showing a consistently higher or consistently lower concentration than the other labs. The actual concentration levels are also shown as a means of comparison. The tendency for all laboratories taken together appears to be to show a low concentration with respect to the true value, at all three concentrations.

B.8 Variance Components From the Nitrate Solution Data

An *analysis of variance* (AOV) was performed on the nitrate solution data to determine what effects are significant contributors to the variability in the analysis. A separate analysis was performed on each set of solution data, and the resulting AOV tables are shown in Table B.10.

The nitrate solution data is laid out in a *two level nested design*. The model for this design is a *random effects model* with

$$y_{ijk} = \mu + \gamma_i + \tau_{j/i} + \epsilon_{k/j/i}$$

TABLE B.7. REPORTED NITRATE SOLUTION CONCENTRATIONS, $\mu g\ NO_2/m\ell$

Collaborator	Day	Repl.	Sol. A	Sol. B	Sol. C
Lab 101	1	1	34.6	6.1	20.1
		2	34.6	6.0	20.2
		3	34.1	5.8	20.1
	2	1	39.6	8.0	24.4
		2	39.9	7.1	21.8
		3	39.6	8.2	24.6
	3	1	36.3	8.6	19.6
		2	37.5	6.6	21.5
		3	37.2	6.0	21.3
Lab 102	1	1	28.0	5.5	20.7
		2	25.5	8.0	12.0
		3	25.0	4.3	18.5
	2	1	41.4	7.8	21.3
		2	41.0	8.6	23.2
		3	39.8	8.2	22.3
	3	1	37.7	5.5	21.5
		2	36.7	6.2	21.5
		3	38.5	6.0	21.5
Lab 103	1	1	43	7.0	24
		2	45	7.0	24
		3	44	7.0	23
	2	1	44	8.0	25
		2	40	7.5	24
		3	42	7.5	23
	3	1	40	6.0	21.5
		2	39.3	6.3	22.5
		3	41.0	5.5	21.5
Lab 104	1	1	37.4	4.8	27.7
		2	38.6	2.2	24.2
		3	37.4	3.7	24.5
	2	1	37.7	4.2	22.8
		2	37.7	3.6	22.8
		3	37.2	4.8	23.5
	3	1	37.5	3.7	22.8
		2	38.6	1.5	23.8
		3	38.5	3.2	22.9

TABLE B.8. LABORATORY DAY AVERAGES FOR NITRATE SOLUTION DATA $\mu g\ NO_2/m\ell$

Collaborator	Day	Sol. A	Sol. B	Sol. C
Lab 101	1	34.4	6.0	20.1
	2	39.7	7.8	23.6
	3	37.0	7.1	20.8
Lab 102	1	26.2	5.9	17.1
	2	40.7	8.2	22.3
	3	37.6	5.9	21.5
Lab 103	1	44.0	7.0	23.7
	2	42.0	7.7	24.0
	3	40.1	5.9	21.8
Lab 104	1	37.8	3.6	25.5
	2	37.5	4.2	23.0
	3	38.2	2.8	23.2

TABLE B.9. AVERAGE LABORATORY NITRATE SOLUTION CONCENTRATION, $\mu g\ NO_2/m\ell$

Collaborator	Solution A	Solution B	Solution C
Lab 101	37.0	6.9	21.5
Lab 102	34.8	6.7	20.3
Lab 103	42.0	6.9	23.2
Lab 104	37.8	3.5	23.9
Actual	38.2	7.2	22.3

where

y_{ijk} is the kth repetition, on day j for collaborator i, $i = 1, \ldots, 4, j = 1, 2, 3, k = 1, 2, 3$

μ is the overall mean.

γ_i is the effect of collaborator i.

$\tau_{j/i}$ is the effect of day j within collaborator i.

$\epsilon_{k/ji}$ is the random error of replicate k for day j in collaborator i.

TABLE B.10. NITRATE SOLUTION DATA ANALYSIS OF VARIANCE

Factor	Sum of Squares	DF	Mean Square	Expected Mean Square	Variance Component
Solution B–Mean = 6.0000					
C	73.9889	3	24.6630	$\sigma_r^2 + 3\sigma_D^2 + 9\sigma_C^2$	$\sigma_{C_2}^2 = 2.4222$
D	22.9044	8	2.8631	$\sigma_{r_2}^2 + 3\sigma_D^2$	$\sigma_D^2 = 0.6846$
R	19.4267	24	0.8094	σ_r^2	$\sigma_r^2 = 0.8094$
Solution C–Mean = 22.2111					
C	71.6022	3	23.8674	$\sigma_r^2 + 3\sigma_{D_2}^2 + 9\sigma_C^2$	$\sigma_{C_2}^2 = 1.4339$
D	86.9800	8	10.8725	$\sigma_r^2 + 3\sigma_D^2$	$\sigma_D^2 = 2.7687$
R	61.5933	24	2.5664	σ_r^2	$\sigma_r^2 = 2.5664$
Solution A–Mean = 37.9417					
C	244.3408	3	81.4469	$\sigma_{r_2}^2 + 3\sigma_{D_2}^2 + 9\sigma_C^2$	$\sigma_C^2 = 3.2386$
D	418.3933	8	52.2992	$\sigma_{r_2}^2 + 3\sigma_D^2$	$\sigma_D^2 = 17.1204$
R	22.5133	24	0.9381	σ_r^2	$\sigma_r^2 = 0.9381$

Then any individual observation, y_{ijk}, is estimated by the equation

$$y_{ijk} = \hat{\mu} + C_i + D_{j/i} + e_{k/j/i}$$

where $\hat{\mu}$, C_i, $D_{j/i}$, and $e_{k/j/i}$ are estimates of μ, γ_i, $\tau_{j/i}$, and $\epsilon_{k/j/i}$, respectively.

The overall mean is presented for each solution across collaborators, along with the mean squares obtained and the expected mean squares for each factor. Using the *expected mean squares*, we are able to derive estimates of the individual variance terms, as well as to determine the correct ratios for the F-tests of interest.

The *F-ratios* are presented in Table B.11, along with their corresponding degrees of freedom and significance levels. Using a significance level of 5 percent, we can evaluate the effect of the factors involved in the analysis. For the *collaborator factor*, a significant effect was detected only at the low concentration, solution B. This results from the values reported by lab 104, which were approximately half those of the other labs.

TABLE B.11. F-RATIOS AND PROBABILITIES

Solution	Factor	DF	F	Significance
B	Collaborator	(3, 8)	8.6141	0.008
	Day/Collaborator	(8, 24)	3.5373	0.009
C	Collaborator	(3, 8)	2.1952	0.18
	Day/Collaborator	(8, 24)	4.2365	<0.005
A	Collaborator	(3, 8)	1.5573	>0.25
	Day/Collaborator	(8, 24)	55.7501	<0.005

The *day within collaborator effect* was significant for all solutions, however. This same occurrence has been reported by Hamil and Camann[3] in a previous study on Method 7 and is an indication that additional variability is introduced into the determinations by the day to day procedural differences in the laboratory. The magnitude of the day component, σ_D^2, was on the same level as the replication component, σ_r^2, for the two lower concentrations and greatly larger for the high solution. Using the nitrate solution data, now, we can obtain estimates of the *between* and *within lab variance* of a Method 7 determination due to the analytical process alone. For σ^2, we use the replicate variance component $\hat{\sigma}_r^2$. For the between-lab component, σ_D^2, however, some modification is necessary to obtain a result consistent with the definitions. For each solution, we obtain a *variance estimate* or mean square, by a similar technique to that used for the test values. The sums of squares are obtained from the differences across collaborators at a given day and replicate number. In notational form, we define

$$MS_b = \frac{1}{9}\sum_{i=1}^{3}\sum_{j=1}^{3}\ \frac{1}{3}\sum_{k=1}^{4}(y_{ijk} - \bar{y}_{ij\cdot})^2 \quad ,$$

where

$$\bar{y}_{ij\cdot} = \frac{1}{4}\sum_{k=1}^{4} y_{ijk}.$$

TABLE B.12. VARIANCE COMPONENTS OF NITRATE SOLUTION DATA

	Sol. B	Sol. C	Sol. A
μ, µg/10 ml	7.2	22.3	38.2
MS_b	3.5706	6.6904	21.3270
σ_b			
Within-Laboratory Variance			
$\sigma^2 = \sigma^2$	0.8094	2.5664	0.9381
σ, µg/10 ml	0.8997	1.6020	0.9686
Laboratory Bias Variation			
MS_L	2.7612	5.0884	20.3584
σ_L	1.6617	2.2557	4.5120

For solutions A, B, and C, the variance components are presented in Table B.12. As before, MS_b estimates $\sigma_L^2 + \sigma^2$, so $MS_L = MS_b - \sigma_r^2$ is the *lab bias component.* The values obtained for the precision estimates are presented in Table B.12 for the nitrate solution data. No justification could be found for applying the coefficient of variation approach to these estimates, as the within lab standard deviation appears independent of the solution concentration level. As a result, the within lab and lab bias components are estimated by alternative techniques and presented in Section III F.

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